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(54) Title: PROCEDURE FOR CONTROLLING HYGROSCOPIC AND PHYSIOLOGIC PROPERTIES OF A FOOD SALT PRODUCT DUE TO POLYVALENT METAL HALIDES CONTAINED THEREIN, AND PRODUCT PREPARED ACCORDING TO THE PROCEDURE AND USE THEREOF

(57) Abstract

The present invention concerns a procedure for controlling the hygroscopic and physiological properties of a food salt product, caused by polyvalent (valency of the cation >1) metal halides contained therein. As taught by the invention, to the solution containing said halides is added material acting as ligand and which becomes linked to said halides, forming an adduct or adducts. The complexing material added is an amino acid or a derivative of such or a compound containing amino acid parts, or a mixture of such. The invention also concerns a food salt produced with the aid of the procedure, and the use thereof.

PROCEDURE FOR CONTROLLING HYGROSCOPIC AND PHYSIOLOGIC  
PROPERTIES OF A FOOD SALT PRODUCT DUE TO POLYVALENT  
METAL HALIDES CONTAINED THEREIN, AND PRODUCT PREPARED  
ACCORDING TO THE PROCEDURE AND USE THEREOF

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The present invention concerns a procedure as defined  
in the preamble to Claim 1 for controlling the hygroscopic and  
physiological properties of a food salt product. The invention also  
concerns a product prepared in accordance with the procedure,  
and its use.

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When producing a food salt product intended to be  
used in various connections, e.g. in preserving foodstuffs, in  
other treatments thereof, in producing processed foods, in pre-  
paring food and in seasoning food, an important aim is nowadays  
avoidance of excessive inclusion of common salt, or sodium chlor-  
ide NaCl, in the formulation of said product; the reason for such  
endeavours is the clearly documented harmfulness of NaCl to  
human health. In order that the desired effects of the food salt  
might be achieved all the same, endeavours are being made to  
replace the sodium chloride, or at least part of it, with other  
mineral salts, e.g. potassium, magnesium and/or calcium chloride.  
The cations contained in these are physiologically desirable other-  
wise as well. It can moreover be considered an advantage of the  
food salt product preparing procedure that there is in connection  
therewith a chance to incorporate in the product, trace substan-  
ces etc. desirable in human metabolism not mentioned in the fore-  
going. Likewise, it is important in view of keeping the product in  
storage that it is substantially homogeneous with regard to its  
various constituents and that no detrimental grading or segrega-  
tion of these constituents is likely to occur during storage. This  
same range of physical properties also encompasses good sprink-  
ling quality of a product meant to be used for table salt, for  
instance.

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When in the food salt preparing process the minerals  
mentioned above are combined with each other and/or with sodium  
chloride, one has to solve in a satisfactory way the problem of  
hygroscopicity induced by them in the end product, either in  
such manner that the product displays no tendency of deliques-

cence at all or so that the product has a specific water binding capacity suited to a particular use. Another significant objective is a taste presented by the food salt product and by the food treated and/or seasoned therewith which pleases the person ingesting the food and generally simulates the flavour of table salt.

Consideration of taste requirements as well as physiological tolerability excludes in practice the use of anions other than chloride (e.g. sulphates, carbonates and possibly some other halides).

Two patent applications have to be cited as references tangent to the field of the present invention: WO A1 93/16117 (A 23 L 1/237), and WO A1 92/19668 (A 23 L 1/237). The first of these references discloses the formulation of table or household salt from sodium and potassium chloride and a magnesium salt; with a view to counteracting the hygroscopicity of the product, the reference teaches to coat the grains of salt mixture with a non-hygroscopic substance. The second reference discloses a way to treat NaCl-K/Mg salts comprising quick drying of the dissolved mix and aiming at producing a stable double salt structure. Products according to either reference fail to meet all the requirements set as objectives for the present invention. The same is true regarding commercially available (Na)-K-Mg table salts, as examples of which the commercial products by name Seltin<sup>™</sup> and Pan Salt<sup>™</sup> may be mentioned.

The state of art comprises a number of references, such as Patents EP A1 59 3631, US A 5,145,707 and US A 4,243,691, according to which in preparing a food salt product to the starting material thereof is added a specified amino acid or equivalent. However, the starting material contains only sodium and/or potassium chloride, whereby these teachings are not encompassed by the generic definition of the present invention. As a matter of fact, the complexing of halides by action of ligand addition as taught by the invention, which constitutes the fundamental idea of the invention, cannot be realized in the case of univalent Na nor K cations.

No food salts containing calcium have been disclosed, nor commercially produced. Additional calcium supply is a highly

significant nutritional factor because of osteoporosis, from which nearly all people suffer in their old age, and women already after their menopause. In certain even extensive regions (e.g. in Japan), calcium deficiency due to diet quality is indeed of pandemic order.

Thus, we have to note that at the present time no food salt containing magnesium and/or calcium is available which would meet the requirements set in the foregoing. The present invention abolishes this defect.

The technique described in the characteristic features part of Claim 1, that is, use of an amino acid or of a compound containing such to produce a complex compound with a metal salt in which the cation is polyvalent (valency  $>1$ ) has been considered in the following references: FSTA AN 75(12):A0660, Journal of Japan Oil Chemists' Society (Yukagaku), (1975)24 (1), 15-21 (Kajimoto et al.); CA AN 105:17145, Zh. Neorg. Khim. (1985), 30(11), 2954-6 (Saleeva et al.); CA AN 117:259179, Zh. Neorg. Khim. (1992), 37(3), 683-7 (Balkunova et al.); and CA AN 107:206125, Talanta (1987), 34(9), 817-20 (Harju).

In these references, the chemical and spectroscopic characteristics of complex compounds produced only with glycine or only with leucine have been investigated, without any mention of the characteristics constituting objects of the present application. The calcium chloride adduct constituting the object of one reference (Balkunova et al.) is intended to serve as poultry raising fodder, and therefore this too falls outside the generic demarcation of the present application.

It follows that use of glycine and/or amino acid derivatives towards controlling the properties of the food salt product in hand is not apparent from the state of art and that it is a novel, inventive insight.

The aim of the invention is to disclose a procedure to be used in preparing a food salt product, thanks to which the end product meets the requirements consistent with the objectives stated in the foregoing.

The procedure of the invention is mainly characterized by that which is stated in the characteristic features part of

## Claim 1.

As taught by the invention, the metal halides meant to be incorporated in the product are brought together, dissolved or in solution in a liquid, such as water, with at least one amino acid or substance comprising amino acid parts, under such conditions (including suitable heating) that said addition will combine with them forming a complex compound, or adduct. This is because it has been found in investigations that adducts of this kind, separated in solid form, meet well the aims which have been set for the invention.

In the simplest case, and at the same time one which is advantageous, said amino acid ligand is glycine, or aminoacetic acid  $\text{H}_2\text{NCH}_2\text{COOH}$ , or leucine. Other amino acids may also be contemplated, although with increasing carbon number solubility problems and other problems are encountered. Also usable are derivatives of amino acids, such as asparagic acid and glutamic acid, and their salts, as well as natural or synthetic polypeptides, proteins, protein hydrolysates and many kinds of mixtures of the aforementioned. The compounds listed in the foregoing are, on the whole, substances associated with human metabolism, and their use in the manner disclosed by the invention, within certain limits, causes no physiological toleration problems. Thus, they can be used when it is desired to devise a food salt formulation with less sodium chloride than before, or with no sodium chloride at all, which may of course be incorporated if desired. When the ligand becomes linked with chlorides of several kinds of cations simultaneously, those aims of the invention will be realized which imply intimate combination of cations. It has especially been borne out by investigations that acceptable flavour of the product, which is an aim of the invention, is excellently achieved as a rule.

According to an embodiment of the invention, the metal chloride material to be treated using the procedure is a mineral containing sodium, potassium, magnesium and/or calcium, e.g.  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (carnallite) or a mixture of sylvinite  $\text{KCl} \cdot \text{NaCl}$  and  $\text{MgCl}_2$ , or equivalent artificial products or mixtures.

The treatment of the invention may be carried out, in order to control the properties of the product, under buffered

conditions, by adding e.g. citric acid, malic acid or tartaric acid.

It is appropriate in industrial applications of the procedure to dissolve the metal chloride components of the product to be prepared, and possibly its other components, one by one or simultaneously e.g. in water and to add the ligand component to the solution thus obtained. One may equally use, for mineral starting material, solutions or brines from a variety of sources, e.g. from natural water bodies, such as the Dead Sea, from geowaters of volcanic tracts, or from industry, containing the desired mineral components in proportions which are consistent with the desired product composition or can be made consistent therewith by applying suitable treatments.

We have now found in investigations that by adducing one molecule, that is with equivalent ratio 1.0 of ligand and metal chloride, good non-hygroscopicity can be achieved. By varying said ratio in limits 0.5...3.0 and by suitable selection of ligand material, it is equally possible to produce food salt having desired water binding capacity (e.g. for requirements in meat processing industry), and to regulate the flavour of the product, for instance.

It is possible in conjunction with the procedure of the invention, advantageously and without effort, to add either in the process step or to the end product, other minerals, compounds and/or trace substances so that the food salt being produced serves as their carrier.

The procedure of the invention is advantageous in cost since it is easy to carry out and does not require major production arrangements or apparatus, and since the consumption of ligand material is only determined by the quantity of material to be complexed; this consumption can be limited by means of selecting said equivalent ratio: investigations have revealed that equivalent ratio about 1.0 is appropriate. In an embodiment of the procedure even greater economy is achievable by substituting for part of the ligand material which would otherwise be needed, e.g. colloidal silicic acid or an equivalent compound participating in complex formation.

The technique of the procedure of the invention, and

results obtained in its investigation, are more closely described with the aid of embodiment examples now following.

#### Example 1

5 In 75 ml water 20.0 g natural carnallite were dissolved, having the following composition (determined by analysis): 0.22 NaCl·0.70 KCl·MgCl<sub>2</sub>·6 H<sub>2</sub>O; this starting material was characteristically a large-crystalline, colourless crystal mass, and it began immediately to deliquesce under influence of air humidity.  
10 The minimal quantity of unsolved material was removed by filtration. To the solution was added, with agitation and heating, L-glycine in quantity equivalent, relative to MgCl<sub>2</sub>, 5.25 g (0.07 mol), thereafter raising the temperature of the solution to 70°C and inspissating the solution.

15 Yield was 23.2 g of crystalline, white product with neutral flavour, in normal conditions completely stable, i.e. not hygroscopic at all.

20 The product of Example 1 is well suited to be used as a constituent of a food salt preparation, for instance on the side of potassium chloride and, possibly, sodium chloride, desirability of both latter constituents being determined by physiological aspects. Substitution of racemic glycine for the L-glycine used in Example 1 produced equal result.

#### Example 2

25 In 100 ml water were dissolved 20.0 g natural carnallite as used in Example 1 and 6.0 g natural sylvinite having composition 0.55 KCl·NaCl. After filtration of the solution, 6.25 g  
30 (0.07 mol) L-alanine were added. The solution was heated to 70°C and inspissated. 24.3 g of crystalline, white, slightly sweet, in normal conditions stable salt product were obtained. This product crystallized somewhat less rapidly than the salt prepared in Example 1.

35 The salt of Example 2 is suitable, as such, to be used for food salt; owing to complete natural provenance of the start-

ing materials, it has higher trace substance content than the salt product of Example 1.

### Example 3

5 A test was carried out as in Example 2, except that, instead of alanine, 9.31 g (0.07 mol) asparagic acid were added. Yield: 27.2 g of crystalline, white salt product with somewhat acid flavour, stable in normal conditions.

10 The salt product of this example has proved well suited for seasoning e.g. fish dishes, either as such or mixed e.g. with the salt of Example 1.

### Example 4

15 To the starting material solution of Example 1 was furthermore added, calcium chloride  $\text{CaCl}_2$  in the form of dihydrate, the amount added being 5% of the magnesium chloride in the solution. 0.945 g (0.0035 mol) glutamic acid were added, and the experiment was continued as in Example 1. The resulting salt product, amounting to 24.5 g, was crystalline, white, and had a slightly acid flavour, somewhat resemblant of meat. It met the requirements set as to stability.

25 In this example, stabilization of physiologically useful and desirable calcium chloride, known to be enormously hygroscopic, was entirely succesful.

### Example 5

30 For this example an amino acid mix was prepared, simulating the amino acid composition of cereal protein, according to following formulation:



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	Amino acid	Quantity, g	Quantity, mol
5	alanine	4.3	0.0483
	arginine	7.6	0.0436
	asparagic acid	12.2	0.0872
	cysteine	1.3	0.0107
	glutamic acid	10.1	0.1298
10	glycine	4.2	0.0559
	histidine	2.6	0.0168
	isoleucine	4.9	0.0373
	lycine	8.2	0.0625
	methionine	1.3	0.0087
15	phenylalanine	5.2	0.0315
	proline	5.1	0.0443
	serine	5.2	0.0495
	threonine	3.8	0.0320
	tryptophan	1.3	0.0064
20	thyrosine	3.8	0.0210
	valine	5.0	0.0427

This mix was moistened, dried and ground in order to ensure homogeneity; its calculated equivalency was 0.00765 eq/g.

The experiment of Example 2 was repeated, using now instead of alanine, the quantity equivalent in relation to  $MgCl_2$  (9.15 g; 0.07 eq) of above amino acid mix. When the solution was cautiously inspissated, aiding with microwave heating, which promoted crystallisation, the result was 27.3 g of crystalline, pleasant flavoured salt preparation, which was stable in normal conditions.

The product of this example is advantageous in use as starting material for herbal and spiced salt preparations.

#### Example 6

The same chloride solution as in Example 5 was used in this experiment, that is 6.0 g sylvinit and 20.0 g carnallite in 100 ml water, to which in this instance the same amino acid mix was added as in Example 5, at half the quantity, that is 4.58 g (0.035 eq), and 1.0 ml of 15% colloidal silicic acid. The solution was cautiously inspissated, using microwave heating, whereby 22.7 g of crystalline, white salt product with pleasant flavour was obtained, which was stable in normal conditions. Redissolving this product in water produced a clear solution.

The clearness of the solution resulting from redissolv-

ing indicates that the silicic acid participated in complex forming.

The embodiment of this example is advantageous when there is a desire to minimize the costs accruing from amino acid consumption. A process according to this embodiment also enables the quantity of trace substances present in the salt preparation to be artificially elevated if desired.

#### Example 7

In 100 ml water were dissolved, like in Example 2, 20.0 g carnallite and 6.0 g sylvinit, these having the composition stated in that example. To the solution were added, with mixing, 5.0 g protein hydrolysate and 1.0 ml 15% colloidal silicic acid. The mixture was homogenized and spray-dried, whereby there was obtained 25.0 g of slightly yellowish salt product with agreeable flavour. By way of trial, herbal salt was prepared from this product by adding 10% dried and ground herbs; this herbal salt displayed satisfactory stability in normal conditions.

#### Example 8

A test equivalent to Example 1 was made in which however to the carnallite solution (75 g) were added, instead of L-glycine, 4.64 g (0.035 mol) N-glycylglycine and 1.0 mol 15% silicic acid. On inspissation of this solution 22.8 g of white, crystalline salt product were obtained, which was stable in normal condition.

The product prepared in this manner can be used for starting material of food salt preparations. The test just described illustrates the effect of dipeptides in the procedure of the invention on product hygroscopicity.

In the foregoing the invention has been primarily described with the aid of embodiment examples. It is obvious to a person skilled in the art that various embodiments and applications may vary within the scope of the inventive idea expressed by the claims following below.

## CLAIMS

5 1. A procedure for controlling the hygroscopic properties and/or physiological properties, such as flavour, of a food salt product, caused by a polyvalent (valency  $>1$ ) metal halide, or halides, contained therein, e.g. magnesium and/or calcium chloride, characterized in that to the starting material containing said halide or halides dissolved in water, is added ligand material containing at least one amino acid or amino acid derivative or amino acid parts; the mixture thus obtained is heated to about 70°C for complexing the added material with said halide or halides, possibly together with other components of the mixture, such as e.g. potassium and/or sodium chloride; and the resulting material is separated in solid form if desired, e.g. by crystallizing or inspissating, or is used in solution form towards nutritive ends.

10 2. Procedure according to Claim 1, characterized in that the complexing material added is glycine or leucine.

15 3. Procedure according to Claim 1, characterized in that the complexing material added is asparagic acid or glutamic acid or a salt of such.

20 4. Procedure according to Claim 1, characterized in that the complexing material added is a dipeptide.

25 5. Procedure according to Claim 1, characterized in that the material added is a protein, such as cereal protein, or a protein decomposition product, such as a hydrolysate of such.

30 6. Procedure according to any one of the preceding claims, characterized in that the equivalent ratio of the quantity of material added to the quantity of metal halide is in the range of 0.5...3.0, advantageously within 1.0...2.0, and most advantageously about 1.0.

35 7. Procedure according to any one of the preceding claims, characterized in that a silicon compound, such as colloidal silicic acid, is used to replace part of the material containing amino acid which is added.

8. Procedure according to any one of the preceding claims, characterized in that in the product being prepared are

incorporated, either in the processing step or thereafter, desired other minerals, compounds and/or trace substances or equivalent.

5 9. Procedure according to any one of the preceding claims, characterized in that acidity regulating substance is added, such as citric acid, malic acid, tartaric acid or a derivative of these.

10 A food salt produced with the aid of a procedure according to any one of the preceding claims.

10 11. The use of a food salt according to Claim 10 in the preparation or preservation or other treatment of a foodstuff or nutritional product, such as a semi-finished food product, prepared food product or food portion.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00068

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: A23L 1/237

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 789565 A (AJINOMOTO KABUSHIKI KAISHA), 22 January 1958 (22.01.58)	1-11
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A	US 5145707 A (THOMAS D. LEE), 8 Sept 1992 (08.09.92), abstract, claims	1-11
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

- \* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

02/04/98

International application No.

PCT/FI 98/00068

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 789565 A	22/01/58	NONE	
US 5145707 A	08/09/92	US 5176934 A	05/01/93